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# Anisotropy of selenium thin film obliquely deposited in vacuum

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The dependence of regular reflectance of thin films of selenium with the thickness and vapour incidence angle has been measured at different wavelengths A difference in reflectance is found between the *positive* and *negative* curves corresponding to the incidence of light from the side of vapour beam and to that from the opposite side This suggests that the surface of a selenium film prepared by oblique incidence evaporation is assymetrical in its structure The anisotropy of electrical resistivity with deposition angle has been studied in air. The difference between the values of resistivity measured in two directions, parallel and perpendicular to the vapour beam can be explained by self shadowing of growing crystallites and the presence of structural defect The presence of geometric anisotropy in films deposited at an oblique angle of incidence is supported by electron microscopic study

## 1. Introduction

Among semiconductors selenium finds the widest applications and in some of these, it is irreplaceable Selenium crystalisis in a trigonal structure and the unit cell of the lattice contains three atoms arranged in the characteristic spiral chain The ratio of the distances between next neighbours in one chain and between two chains of selenium is about 1·49 (Cooper 1969) The trigonal selenium thus possesses strong anisotropy of the structure and has a number of peculiar and interesting physical properties A peculiar feature of the band structure of selenium is an energy gap which exists between two groups of valence bands This gap leads to a minimum in the spectra at high energies, the main optical anisotropy is also located at high energies The electrical conductivity of selenium depends on the crystal direction Parallel to the $c$-axis the conductivity is greater than perpendicular to it. The ratio $R_{\perp}/R_{\parallel}$ is found to be between the values 3 and 10

Selenium films have been prepared from the vapour by a number of workers, the structure of these films depends upon deposition variables such as substrate material and substrate temperature (Tauraitiene & Tauraitus 1969, Viscakas *et al* 1969, Herd & Chaudhari 1973) However, very little is known about the effect of oblique incidence on the structure and the physical properties of selenium films It is well known (Konig & Helwig 1950) that an obliquely incident film reveals chains of crystallites whose long axes are oriented perpendicular to the direction of vapor beam. The oriented chains give rise to macroscopic effects anisotropy in photovoltage and photo conductivity (Kamiyama *et al* 1962), magnetic anisotropy (Konig & Helwig 1950, Smith *et al* 1960), optical anisotropy (Nakai 1963, Tanaka & Takahashi 1963) and anisotropic resistance (Haraki 1963, Takahashi *et al* 1971, Jain *et al* 1975). The presence of microscopic geometric anisotropy in oblique incidence films may thus be studied from macroscopic measurements In the present study the dependence of regular reflectance with the thickness and vapour incidence angle was measured at different wavelengths The change in the resistivity in selenium films with thickness and deposition angle was also measured in air The experimental results are discussed on the basis of self shadowing effect

## 2 Experimental Procedure

Selenium films were prepared on to corning-7059 glass substrate by evaporation of polycrystalline pure Se from a Tantalum boat in a vacuum of about $10^{-5}$ Torr The geometrical arrangement of the source and the substrate is shown in figure 1. The film thickness was monitored using Fizeau's interfero-

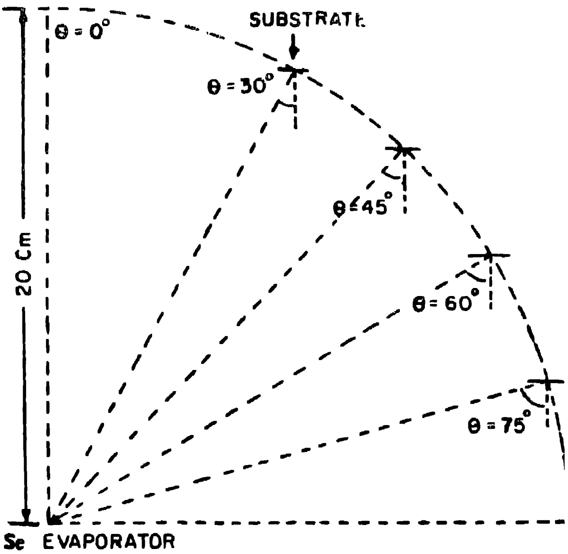



**Fig.1 Schematic illustration of oblique deposition [Angle θ is the deposition angle; $R_{\parallel}$ is the parallel resistivity; $R_{\perp}$ is the perpendicular resistivity]**

Fig. 1

meter method. The substrate was kept at room temperature (27°C), the deposition angle was varied from 0° to 75° with an interval of 15°.

Reflectance of the films were determined as a function of angle of incidence between 20° and 70° at different wavelengths using the interference filters and polarizers. The schematic diagram of reflectivity apparatus is shown in figure 3 which essentially is a research spectrometer fitted with polaroides. The light source was a high pressure mercury vapour lamp and detector was a 1P28 tube The sample mount was in the form of a window, being capable of rotating in vertical and horizontal planes

The geometry of the sample for electrical measurements is shown in figure 2. Large area ohmic current-voltage contacts of evaporated aluminium were made

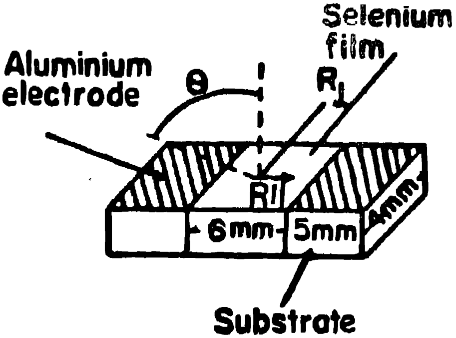
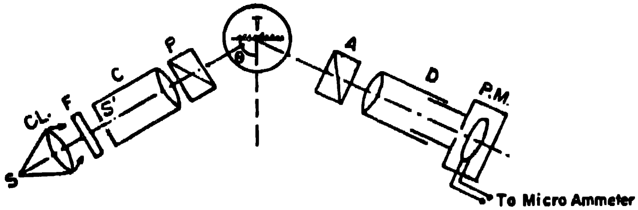



Fig. 2




Schematic representation of reflectometer

S = Source of light ; C L. = Condensing lense

F = Filter ; C = Collimator ; P = Polarizer ;

T = rotating Table ; A = Analyzer ; D = telescope ;

P.M. = Photo multiplier Tube .

Fig. 3

at the end of the selenium films. The spacing between aluminium electrodes was 6 mm and the lateral dimension of the film was 4 mm. Resistivity measured along the direction parallel to the incidence plane of vapour beam shall be called 'parallel resistivity' and expressed as $R_{\parallel}$. In perpendicular direction 'perpendicular resistivity' is expressed as $R_{\perp}$.

To measure the resistance of the film, the current through the specimen was measured using an Electrometer Amplifier (BARC model EA810A) of range $10^{-6}$ to $10^{-12}$ amperes. The d.c. biasing of the sample was done using an electronically regulated d.c. supply (Philips make) of range 250-2500 volts.

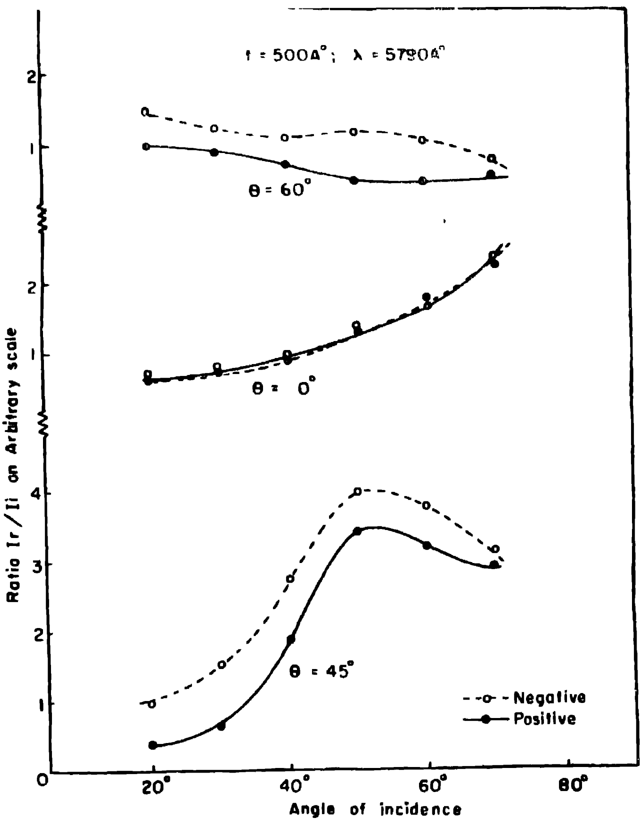



Fig. 4

## 3 Results and Discussion

### A *Reflectance of Selenium Films*

Figures 4, 5 and 6 show the relation between the reflectance and the incidence angle of light, $\theta$ is the angle of incidence of the vapour beam and $t$ is the thickness

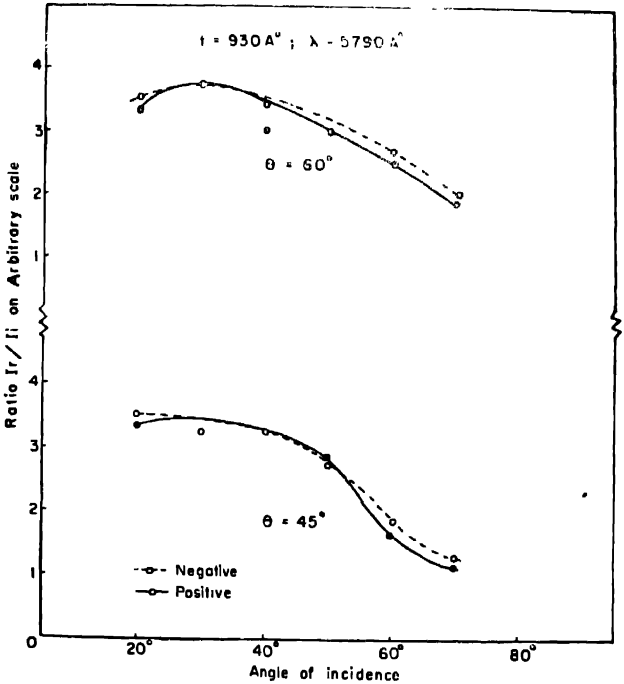



Fig. 5

of the film. In these figures the notation *positive* corresponds to the incidence of light from the side of the vapour beam, *negative* to that from the opposite side. A difference in reflectance is found between the *positive* and the *negative* curves for low thicknesses and large deposition angle This suggests that the surface of the selenium film prepared by oblique incidence evaporation is asymmetrical in its structure. The asymmetry decreases with increasing film thickness and increases with angle of deposition and the same can be explained by the 'selfshadowing' that occurs during the oblique deposition The growing crystallites prevent the impinging atoms from reaching the substrate where the crystallites cast shadows leaving undeposited areas there Hence, in forming a film, all the crystallites grow long, crosswise to the direction of deposition When the deposition angle is large, the crystallites grow more inclined, thereby developing large asymmetry in their shape Further, no detectable difference in reflectance is found between the *Positive* and *Negative* curves for thicknesses larger

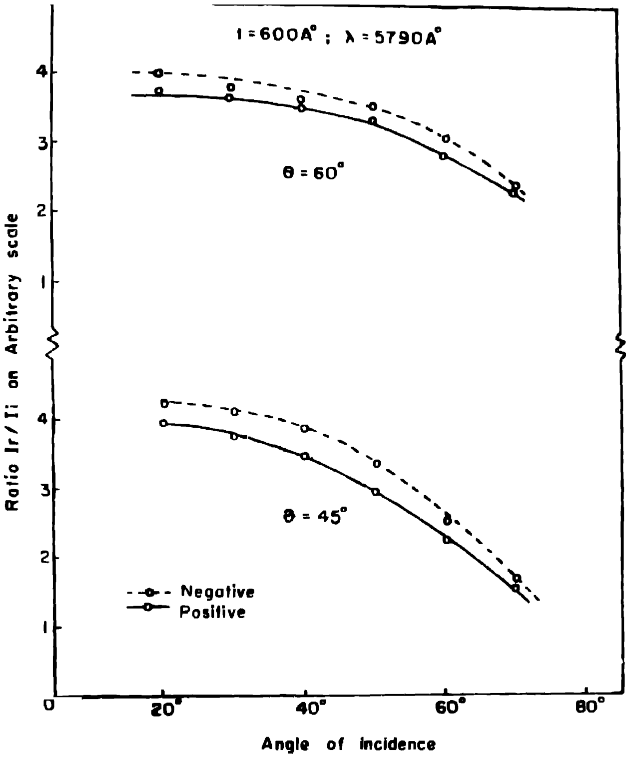
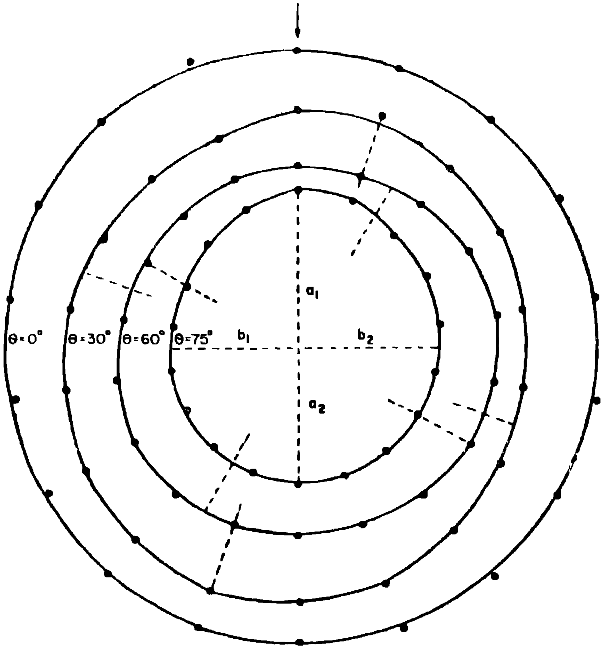



Fig. 6

than 1000 Å Such an effect is expected in view of the following : As the film becomes thicker, the space between the crystallite chains gets filled and as a consequence assume symmetrical shape making the surface of the film almost optically flat The film deposited at 0° angle of deposition and of thickness 500 Å does not show the above effect. Thus it appears that the surface of the film prepared by normal evaporation ($\theta = 0°$) possesses reflectance symmetry.

It is also observed that if the illumination is made by the polarised light, the intensity of reflected light rests with the orientation of the electric Vector relative to the direction of the vapour beam which implies that the reflectivity of the film has different values in two directions, parallel and perpendicular to the direction of deposition. Figure 7 shows the variation of reflectivity of the sample of thickness about 600 Å with the orientation of the electric vector of




Reflectivity as a function of Orientation of the Electric Vector

Fig 7

the incident plane polarised light relative to the direction of the vapour beam. From these curves, it follows that at 0° deposition angle the curve is symmetrical and is a circle As the deposition angle increases, the curve develops asymmetry with unequal radii along some diameter We measure this anisotropy by the ratios $a_1/a_2$ and $b_1/b_2$, where $a$'s and $b$'s stands for the radii along two mutually perpendicular diameters and are being plotted as a functioon of deposition angle in figure 8 It follows from the graph that the ratio $b_1/b_2$ is almost independent of angle of deposition while the ratio $a_1/a_2$ increases with the angle of deposition This may be explained by 'self shadowing' described earlier

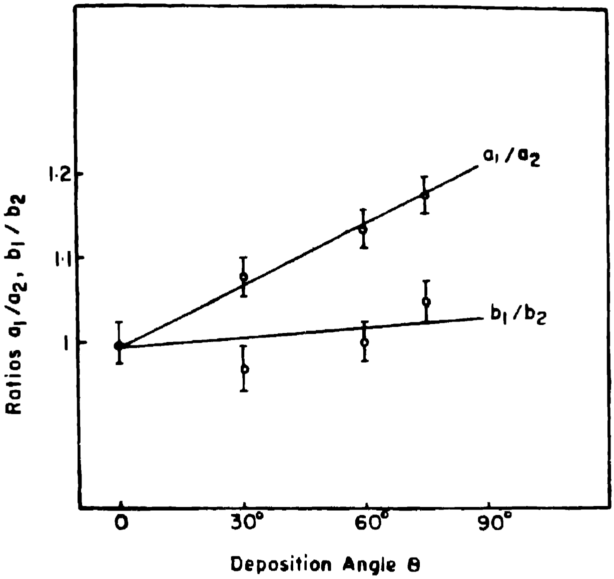



Fig 8

Figure 9 shows the reflectivity of the selenium film of thickness 1050Å, being deposited at an angle of 15° as a function of angle of incidence of light at different wavelengths It is seen that the magnitude of the reflectivity decreases with decreasing wavelength The reflectivities ($R$) are being calculated using the following expression,

$$\frac{I(r)}{I(i)} = \frac{4R \sin^2 \delta/2}{(1-R)^2 + 4R \sin^2 \delta/2}$$

$$\delta = \frac{4\pi}{\lambda} t \sin i.$$

where $I(r)$ and $I(i)$ are the intensities of reflected and the incident beams, $\lambda$ is the wavelength of the light used, $i$ is the angle of incidence and $t$ is the thickness of the film The observed effect follows the above expressions

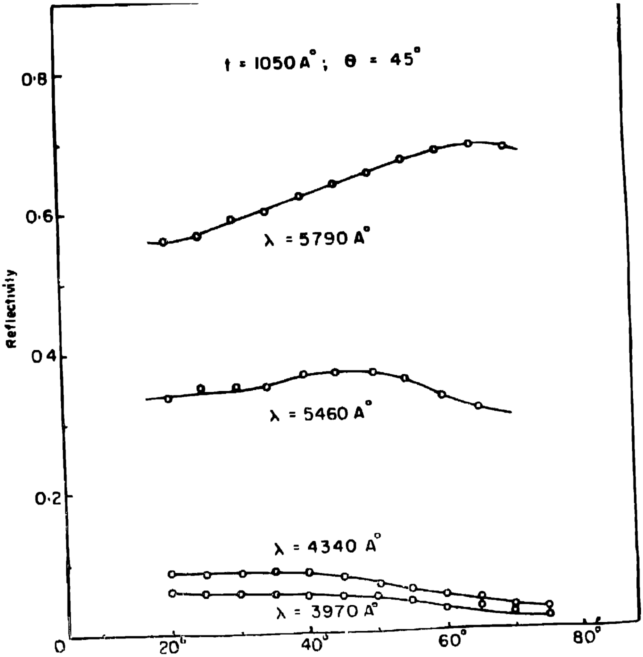



Fig. 9

**B** *Resistivity Anisotropy*

Figure 10 shows the dependence of the observed parallel and perpendicular resistivities ($R_{\parallel}$ and $R_{\perp}$) of the film with deposition angle $\theta$ before and after annealing at 40°C for 30 minutes. This figure shows that the parallel resistivity for lower thickness (550 Å) decreases with the increasing angle of deposition while the same for thicker film ($t$ = 1600 Å) has a constant value with deposition angle. Such an effect is expected in view of the following. As the film becomes thicker, the space between the crystallites chains gets filled and as a consequence the crystallites touch each other almost continuously, therefore $R_{\parallel}$ becomes independent of deposition angle for thick films. The same has been observed earlier through optical measurements. It is interesting to note that an opposite trend is observed for perpendicular resistivity i.e., the resistivity is independent of deposition angle for films of lower thicknesses and varies with $\theta$ for higher thicknesses An obliquely deposited thin film has chain structure with its long axis perpendicular to the beam direction The self shadowing effect is expected to be minimum along the direction perpendicular to the vapour beam Thus variation of $R_\perp$ with deposition angle $\theta$ should be much less than that of $R_\parallel$. The experimental results also seem to be in accordance with the above picture.

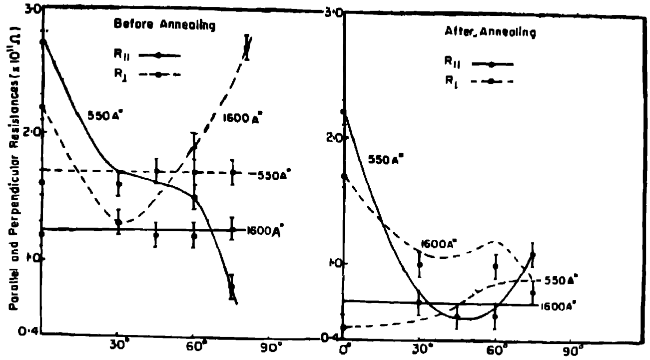



Fig 10

The observed variation of $R_\parallel$ for thin films and $R_\perp$ for thick films with deposition angle $\theta$ may possibly be attributed to the structural defects, being developed in the films during deposition . the structural defects density is assumed to have a direct relation with the angle of deposition. To explain the above variation, let us consider the formula for the conductivity

$$\sigma = ne\mu,$$

where $n$ is the carrier density, $e$ is the electronic charge, and $\mu$, the mobility. Thus, the conductivity for a given thickness increases if $n$ and/or $\mu$ increases. For small thicknesses, one generally expects that an increase in the number of defects will increase the carrier density but will decrease the mobility.

As the selenium films generally show the $p$-type conductivity, one expects that an increase in acceptor sites due to defects will increase the carrier density $n$ but will decrease the mobility $\mu$ An increase in $\mu$ may also arise from an increase in grain size which is expected to be enhanced by self shadowing The observed increase in conductivity with deposition angle may thus be accounted for the increased grain size The effect of annealing on the resistivity of the film is depicted in figure 10 Annealing reduces the number of defects and, therefore, $n$. The reduction in defects together with the increased grain size both tend to increase $\mu$ The observed increase in conductivity associated with the change to the annealed state thus results primarily from an increase in $\mu$.

Ratios $R_\perp/R_\parallel$ are plotted against the deposition angle as shown in figure 11. It is found that with an increase in deposition angle, anisotropy in resistivity increase for thin films and decreases for thicker films. The effect is found to reduce after annealing the film. The observed trend is in accordance with the above picture. Further, for a film of thicker 1000 Å, deposited at 0°, the ratio is found to be about 2 which is in good agreement with the value for the bulk selenium (Cooper 1969).

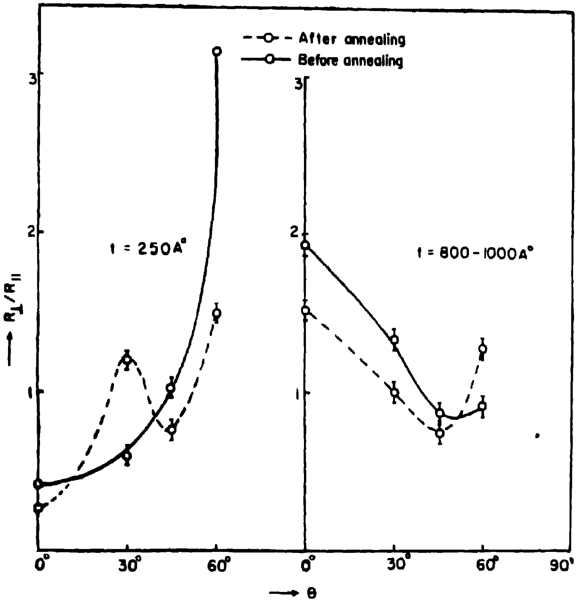



Fig 11

Figure 12 shows the electron micrograph of the film of thickness 300 Å deposited at an angle of incidence of 75° In this the agglomeration of crystallites into chain whose long axes are on the average perpendicular to the beam direction can be inferred. It thus provides direct evidence that geometric anisotropy on a microscopic scale exists in oblique-incidence selenium films and leads to an interpretation to the origin of anisotropy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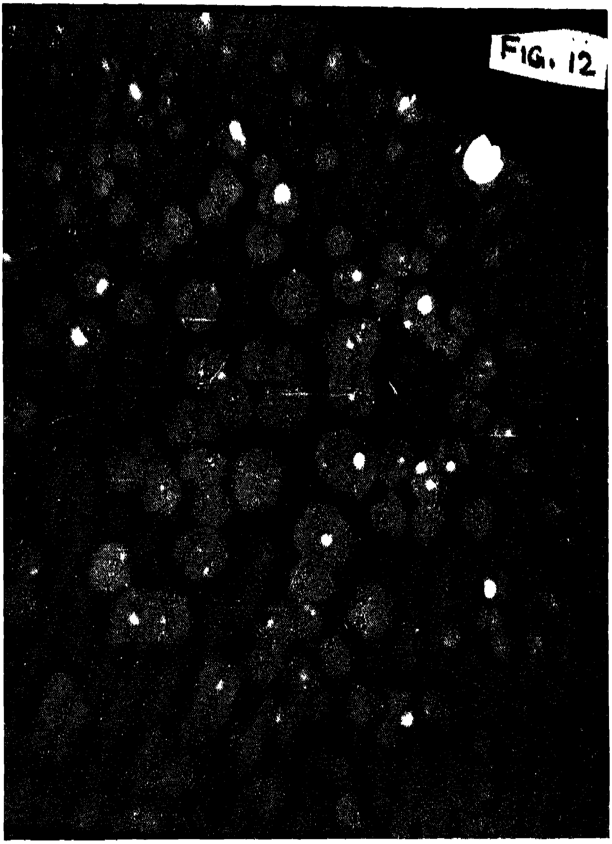


Fig 12

operation extended by Dr O N. Srivastava at B H U, Varanasi in the use of electron microscope is gratefully acknowledged

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